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SURFACE MODIFICATION AND IMPROVED ADHESION OF WOOD-PLASTIC COMPOSITES (WPCs) MADE WITH DIFFERENT POLYMERS BY TREATMENT WITH ATMOSPHERIC PRESSURE ROTATING PLASMA JET

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Abstract

Because of the low polarity of the polymers used for manufacturing wood plastic composites (WPCs), they have low surface energy and their adhesion properties are limited. In this study, the surface modification with atmospheric pressure rotating plasma jet (APPT) of several WPCs made with different polymers is proposed as an environmentally friendly alternative for increasing their hydrophilicity and adhesion. Both the nozzle-WPC surface distance and the platform speed were varied during APPT treatment and only one pass was carried out. APPT treatment of the WPCs made with polyethylene and polypropylene removed most of the wood component and exposed the polymer to the surface, changing their chemistry, surface energy and topography. An improvement in adhesion of the WPCs to different coatings was obtained which was ascribed to the creation of new polar carbon-oxygen moieties, and the removal of wood component on the WPC surfaces. The less surface modification caused by APPT treatment of the WPC made with poly (vinyl chloride) was ascribed to its low wood content and the presence of inorganic fillers.

Keywords: A. Adhesives for wood, B. Wood, B. Surface treatment by excited gases, C. Thermal analysis.

1. INTRODUCTION

During the last few years there has been a noticeable interest in developing wood plastic composites (WPCs) as substitutes for wood materials due to their higher mechanical properties and excellent outdoor performance. WPCs are commonly used in the building, furniture, and automotive industries, and find widespread applicability in decking materials and materials for railing, siding and panelling, materials in which high outdoor resistance is mandatory. WPCs are made of wood fibres, polymers and additives. The most common polymers used for manufacturing the WPCs are polyethylene (PE), polypropylene (PP) and poly(vinyl chloride) (PVC), and, in general, they account for 30-70wt% of the total mass. The WPCs also contain around 5wt% of additives (biocides, lubricants, ultraviolet light stabilizers…) for facilitating processing and improving the interfacial wood-polymer interactions [1]. Because of the low surface energy of PE and PP, the surfaces of the WPCs made with these polymers are nonpolar and, therefore, they are difficult to decorate, paint, apply coatings, and bond with adhesives.

Currently, WPC materials are joined by means of nails or mechanical interlocking, but these methods cannot be easily used in materials with irregular geometrical shape; currently, WPC materials are mechanically anchored to metallic structural networks fixed on the substrate surface [2]. On the other hand, for imparting colour, colorants and dyes must be incorporated during WPC manufacturing and processing, this limiting their applications. For avoiding these limitations, different chemical and physical surface treatments of WPC materials have been proposed with the aim of increasing their surface polarity and adhesion.

Previous studies showed that treating the surface of different WPCs with flame, water, sanding, chromic acid, and corona discharge improved notably their adhesion properties [1,3-4]. The surface treatment with chromic acid was the most effective but it has to be substituted because of environmental concerns. In a recent study [5], four environmentally friendly surface activation pre-treatment methods to improve adhesion of WPCs made with PP to epoxy adhesives have been proposed, including hydrogen peroxide solution, hot air, flame, and halogen heating lamps, and improvements in adhesion of 37-44% were obtained. On the other hand, it has been shown that the treatment of different WPCs with corona discharge improved their paint ability and enhanced their bonding properties [6]. More recently, new surface treatments have been proposed for increasing the hydrophilicity of different WPCs. Thus, Gupta et al. [7] proposed the surface treatment of different WPCs with benzophenone activated with UV radiation and with low-pressure oxygen plasma, and found that the treatment with low-pressure oxygen plasma improved notably their wettability and adhesion [7]. Furthermore, the treatment with low-pressure plasma of WPC made with PP for improving adhesion have been demonstrated useful [8]. However, although effective, the treatment of WPCs with low-pressure plasmas is difficult to apply on an industrial scale because of the need of a vacuum, the treatment is discontinuous, and it is limited to small pieces. Therefore, recent efforts have been devoted to developing surface treatments with atmospheric pressure plasmas which lack these limitations. The advantages of the treatment of WPC with atmospheric pressure plasmas rely on being ecological and environmentally friendly, they are effective and fast, they can be easily automated, and large and irregular pieces can be treated.

Recently, studies on the treatment with dielectric barrier discharge (DBD) of WPCs made with PE and PP have been published [9-12], and they concluded that the improved adhesion was ascribed to the increase of the surface energy and wettability of the WPC surfaces. To the best of our knowledge, there is one paper [13] only in the existing literature dealing with the surface treatment of WPC with atmospheric plasmas. Oporto et al. [13] treated WPCs made with PP with a forced air plasma surface treater unit for improving their adhesion, and the distance between the plasma source and the WPC surface was varied between 1 and 2 inches only, and 5-10 passes of the WPC surface over the plasma stream were needed to be effective.

In recent years the use of cold plasmas produced with atmospheric plasma torches or jets which operate under a non-thermal equilibrium state have been revealed as promising alternative surface treatments to other atmospheric plasma treatment units [14]. Furthermore, the atmospheric plasma jets are more versatile than other atmospheric plasma sources as different substrates with any shape or size can be treated. Hämäläinen and Kärki [15] treated WPC made with PP with a FG5001 plasma jet provided with a RD1004 plasma head in which the WPC surface-plasma source distance was fixed to 9 mm and treatment times of 3 and 5 seconds were used only. In this study, surface treatment with an atmospheric pressure rotating plasma jet (APPT) of WPCs prepared with different polymers (PE-WPC, PP-WPC, and PVC-WPC) for improving their surface energy and adhesion was carried out; one pass only of the plasma head over the WPC surface was carried out, the APPT treatment conditions were varied widely and optimized, and the adhesion of the WPCs to coatings of different nature were evaluated.

2. EXPERIMENTAL

2.1. Materials

Three commercial WPCs prepared with different polymers (polyethylene, polypropylene and poly (vinyl chloride) were used:

- PE-WPC. It is a commercial wood flour filled high density polyethylene (HDPE) composite made by extrusion that was supplied by Condepols (Jaen, Spain). PE-WPC material was received in the form of alveolar boards and it was cut into pieces of 3x7 cm^2 for characterization, surface modification and adhesion tests.
- PP-WPC. It is a commercial wood filled polypropylene composite supplied by SCT-Straw (Barcelona, Spain). PP-WPC material was received in the form of solid profiles and it was cut into pieces of 4x4 cm^2 for characterization, surface modification and adhesion tests.
- PVC-WPC. It is a commercial composite made with vegetable fibres and PVC that contains mineral inorganic fillers and was supplied by Plásticos Viters S.A. (Valencia, Spain). PVC-WPC material was received in the form of solid profiles and was cut into pieces of 3x7 cm^2 for characterization, surface modification and adhesion tests.

2.2. Surface treatment with APPT

APPT treatment of the WPCs was carried out with an FG1001 plasma generator (Plasma Treat GmbH, Steinhagen, Germany) provided with a rotary nozzle with an opening ring of 4 mm diameter and an angle shot of 14º. Compressed synthetic air (Air Liquide, Madrid, Spain) was used for generating

the atmospheric plasma. The atmospheric plasma was generated by using 300 V voltage and 8.6 A current, and the pressure of the compressed air was set to 2.5 bars. The WPC surface-nozzle distance was varied between 1 and 3 cm, and the treatment time was varied by changing the speed of the electronically controlled platform on which the WPC was placed between 0.5 and 8 m/min (Figure 1).

2.3. Experimental techniques

IR spectroscopy. The chemical modifications of the WPC surfaces produced by APPT treatment were assessed by attenuated total reflectance infrared spectroscopy (ATR-IR) in a Tensor 27 spectrometer (Bruker Optiks, Ettlingen, Germany) using a diamond prism. 60 scans were recorded and averaged with a resolution of 4 cm^{-1}. The incidence angle of the IR beam was 45º.

IR spectroscopy was also used for characterizing the chemistry of the WPCs and for calculating their "wood index" values. In a previous study the "wood index" obtained from the IR spectra of the WPCs was proposed as a typical parameter for characterizing their wood content [16]. The "wood index" was defined as the ratio between the intensities of the –O-C-O- band at 1023 cm^{-1} and the band of methylene groups at 2912 cm^{-1} (Eq. 1) :

$$\text{Wood index} = (I_{1023}/I_{2012}) \times 100 \quad \text{(Eq. 1)}$$

Thermal gravimetric analysis (TGA). The compositions of the commercial WPCs were determined by TGA. 10 mg of WPC were placed in the platinum crucible of a TGA TA Q500 instrument (TA instrument, New Castle, DE, USA) and heated from room temperature up to 800 ºC in a nitrogen atmosphere (flow: 60

ml/min) by using a heating rate of 10 ºC/min. Once 800 ºC was reached, the nitrogen gas was changed to air (flow: 60 ml/min) and maintained isothermally during 15 minutes for removing all organic ashes and for determining the existence of inorganic fillers in the WPCs.

Contact angle measurements. Contact angle values at 25 ºC of different test liquid drops placed on the as-received and APPT treated WPC surfaces were determined using a Ramé-Hart 100 goniometer (Netcong, NJ, USA). 4 µl drops of bidistilled and deionised water (polar liquid) and diiodomethane (non-polar liquid) were placed on the WPC surface, and the contact angle values were measured immediately after drop deposition. Advancing and receding contact angles were measured using the tilting plate method. Because of the contact angle values obtained by the sessile drop method agree well with the advancing contact angle values, the advancing contact angle value was considered as representative of the surface property of each WPC. At least five drops of each liquid were placed at different locations of the same WPC surface and the measured contact angle values were averaged.

Once the contact angle values on the WPC surfaces were measured, the total surface energy (γ_s) and their polar (γ_s^p) and dispersive (γ_s^d) components were obtained by applying the Owens-Wendt approach (Eq. 2):

$$\gamma_S = \gamma_S^d + \gamma_S^p$$

$$(1+\cos\theta_i)(\gamma_i{}^d + \gamma_i{}^p) = 2(\sqrt{\gamma_i{}^d \gamma_S{}^d} + \sqrt{\gamma_i{}^p \gamma_S{}^p} \qquad \text{(Eq. 2)}$$

where γ_i is the surface tension of the test liquid used for measuring the contact angle, and θ_i is the contact angle value measured with each test liquid; the

superscripts *d* and *p* indicate the dispersive and polar components of the surface tension of the test liquid or the surface energy of the WPC. Two liquids were used to determine the polar and dispersive components of the surface energy of the WPCs, one a polar liquid - water (γ_i^P = 51 mN/m, γ_i^D = 21.8 mN/m) -, and another, a non-polar liquid - diiodomethane (γ_i^P =0 mN/m, γ_i^D =50.8 mN/m).

Scanning electron microscopy (SEM). The surface topography of the as-received and APPT treated WPCs was determined in a Jeol JSM-840 microscope (Jeol Ltd., Tokyo, Japan) working at 15 kV. For improving contrast, before analysis the WPC surfaces were gold coated in Au/Pd Balzers metallizer SCD 004 (Oerlikon Surface Solutions, Balzers, Liechtenstein).

Adhesion measurements. The intrinsic adhesion of the as-received and APPT treated WPCs was obtained from 180º peel tests of WPC/Magic Scotch® acrylic adhesive tape joints in a TA-XT2i texture analyser (Stable Micro Systems, Godalming, UK) by using a peeling rate of 10 mm/s. Magic Scotch® acrylic adhesive tape (3M, St. Paul, MI, USA) was used for determining the extent of the improvement in adhesion in the joints made with APPT treated WPCs, avoiding the influence of the solvent and/or the chemical characteristics of the adhesives and coatings. Pieces of the as-received and APPT treated WPCs of different dimensions (3 x 7 cm^2 for PE-WPC and PVC-WPC; 4 x 4 cm^2 for PP-WPC) were joined to pieces of adhesive tape of 1.9 cm width and 15 cm length. The adhesive tape was applied over the WPC surface and 30 consecutive passes with a rubber roller of 1 Kg were carried out for allowing intimate contact between the WPC surface and the adhesive tape.

On the other hand, the adhesion of the joints made with APPT treated WPC and several coatings of a different nature were determined using the cross hatch test according to ASTM D3359 standard. A multi-blade cutting device 0302001 (Neurtek Instruments S.A., Eibar, Spain) was used for making 6 parallel cuts on the coating in a perpendicular direction to the surface; afterwards, Tesa® adhesive tape was applied on the coating squares made by the cutting device, and the tape was pulled out from the coating surface accounting for the number of removed coating squares. Three replicates were tested and averaged for obtaining the cross-hatch adhesion value. The adhesion values were ranked according to the scale given in ASTM D3359 standard that it is summarized in Figure 2. A cross hatch adhesion value of 5B means excellent adhesion, i.e. all coating squares remain on the coated WPC surface -, and a cross hatch value of 0B means poor adhesion, i.e. the most coating squares detached from the WPC surface.

Two coatings of different chemical nature were applied to the surfaces of the as-received and APPT treated WPCs:

- Sintex MS-35 Plus silane modified polyurethane adhesive (Quilosa-Selena Iberia, Madrid, Spain). The polyurethane was applied with a spatula controlling its thickness on the WPC surface for obtaining a film of about 150 µm. The polyurethane coated WPC was allowed to cure at room temperature for 4 weeks before the cross hatch adhesion test was carried out.

- Caryal R-1 poly(vinyl) acetate adhesive (Paniker S.L., Barcelona, Spain). The adhesive was applied with a brush and the coating thickness was

adjusted with a metering rod of 200 µm. The adhesive coated WPC was allowed to cure at room temperature for 1 day before the cross hatch adhesion test was carried out.

3. RESULTS AND DISCUSSION

3.1. Characterization of the as-received WPCs

The as-received WPCs were commercial materials and their surface properties were characterized for determining the modifications produced by the APPT treatment.

The chemical compositions of the as-received WPCs were characterized by ATR-IR spectroscopy. Under the experimental conditions used in this study, a surface depth of WPC of about 10-15 µm was analysed. The ATR-IR spectra of the as-received WPCs are shown in Figure 3. All ATR-IR spectra show similar bands corresponding to the wood component in the WPC but they differ in the bands corresponding to the different polymer matrices. Thus, the bands corresponding to the wood component appear at 3340-3350 (broad band of the OH group), 1630-1640 (stretching band of the C-O-C group), and the band at 1023 cm^{-1} (the most intense band due to the -O-C-O- group); these bands are more intense in the WPCs made with PE and PP indicating that they contain higher amounts of the wood component than PVC-WPC. On the other hand, all ATR-IR spectra show the C-H stretching bands at 2842-2918 cm^{-1} and the asymmetric and symmetric bands of CH_2 groups at 1375 and 1455 cm^{-1} respectively, all corresponding to polymer hydrocarbon chains. Furthermore, the ATR-IR spectrum of the PP-WPC shows the stretching band of CH_3 groups at 1376 cm^{-1}, and the ATR-IR spectrum of the PVC-WPC shows the C-Cl bands at

1420 (C-H groups in PVC) and 870 cm^{-1}. Therefore, the chemical composition of the as-received WPCs corresponds to lignocellulosic material compounded with polyethylene (PE-WPC), polypropylene (PP-WPC) and poly (vinyl chloride) (PVC-WPC).

A comparison of the intensities of some bands in the ATR-IR spectra of the WPCs provides qualitative information on their different wood contents. Thus, the intensities of the bands of the $–CH_2-$ groups in the ATR-IR spectrum of the PP-WPC are higher than in the one of PE-WPC indicating higher wood content in PP-WPC; furthermore, the noise in the ATR-IR spectrum of the PE-WPC evidences surface roughness. The wood contents of the as-received WPCs were quantified by means of the "wood index" [16], and the obtained values are shown in Table 1. The highest wood index value corresponds to PE-WPC, i.e. the WPC with a lower amount of polymer, and the lowest one corresponds to PVC-WPC.

The compositions of the as-received WPCs were also analysed by TGA. The variation of the weight as a function of the temperature of the as-received WPCs is given in Figure 4, and the weight losses and the temperatures of the different thermal decompositions are given in Table 2. All WPCs show the same three thermal decompositions, except PVC-WPC that exhibits an additional one at 684ºC due to carbon dioxide evolution caused by the decomposition of the carbonate filler in its formulation. It has been shown elsewhere [17] that the TGA thermogram of carbonates showed one unique typical decomposition at 550-750ºC which was ascribed to decomposition of the carbonates producing carbon dioxide. Because a 6wt% loss is considered due to carbon dioxide, the amount of calcium carbonate in PVC-WPC is around 14wt%. The thermal

decompositions of the as-received WPCs correspond to water removal (maximum temperature of decomposition at 31-159ºC – Table 2), decomposition of the wood component (maximum temperature of decomposition at 279-345ºC), and decomposition of the polymer component (maximum temperature of decomposition at 441-454ºC). In general, the weight loss in PP-WPC and PE-WPC corresponding to each thermal decomposition is nearly the same, indicating very close composition; however, the temperature of maximal decomposition of water is much higher and that for the wood component is somewhat lower in PP-WPC, indicating different extents of interactions between the OH groups of the wood fibres in PE-WPC and in PP-WPC. On the other hand, PVC-WPC shows decompositions due to water, wood, PVC, and carbonate filler. In fact, at the end of the WPC TGA experiments carried out in a nitrogen atmosphere, a residual mass of 14-31wt% is obtained (Table 2), and the highest residual mass corresponds to PVC-WPC. For evidencing the existence of inorganic fillers in the WPCs, at the end of the TGA experiments (at 800ºC) the nitrogen was changed to air and maintained isothermally during 15 minutes, and the final residual masses in PP-WPC and PE-WPC are null, whereas a residue of 17wt% is obtained in PVC-WPC, confirming the existence of relative important amount of inorganic fillers in its formulation. These fillers are calcium carbonate (about 14wt%) and, likely, talc (about 3wt%) as they are the two most common mineral reinforcements used in the manufacturing of PVC-WPCs [18].

The topographies of the surfaces of the as-received WPCs were analysed by SEM. Figure 5 shows SEM micrographs of the WPCs at two different magnifications. Whereas the outermost surface of the PVC-WPC is quite

smooth and scarce spots and holes are seen occasionally, the surfaces of the PE-WPC and the PP-WPC are rough because of the wood fibres exposed at the surface. On the other hand, the external surface of the PVC-WPC is covered by a poly(vinyl chloride) layer whereas some filaments of polymers between the wood fibres can be distinguished in the other WPCs. None of the as-received WPCs show evidences of lubricants on their surfaces.

Because the Owens-Wendt approach has been widely used for surface free energy calculations and has been demonstrated to be sensitive to changes in the polarity of polymers, it was used in this study for comparing the surface energies of the as-received WPCs. The contact angle values and the surface energies of the as-received WPCs are shown in Table 3. Because of the existence of non-polar polymer on the WPC surfaces, the water contact angles are high (83-111º) particularly in PE-WPC and PP-WPC. Consequently, the surface energies of the WPCs are low (26-39 mJ/m^2), the lower surface energy values correspond to PP-WPC and PVC-WPC. Whereas the contribution of the dispersive component of the surface energy is the only component that exists in both PE-WPC and PP-WPC, the surface energy of PVC-WPC has contributions from both the polar and dispersive surface energy components. Considering the surface energy value of PVC polymer, the surface energy of PVC-WPC (28 mJ/m^2) is lower than expected. According to Table 3, the water contact angle of PVC-WPC is the lowest among the as-received WPCs (although near 90º) but the high value of the diiodomethane contact angle suggests the existence of a nonpolar moiety (likely talc) on the surface.

3.2. Surface treatment of the WPCs with APPT

The WPC surfaces were treated with APPT to enhance hydrophilicity and improve adhesion. In order to optimize the experimental conditions of the APPT treatment, PE-WPC was selected, and the treatment time (i.e. the speed of the platform on which the WPC is placed for the treatment) and the WPC surface-nozzle distance were varied.

During APPT treatment, the WPC surface-nozzle distance was varied between 1 and 3 cm, and no surface modifications were produced for distances higher than 1 cm. Therefore, the WPC surface-nozzle distance was set to 1 cm in agreement with a previous study [15].

The speed of the platform during APPT treatment of PE-WPC was varied between 0.5 and 8 m/min, the WPC surface-nozzle distance was set to 1 cm, and only one pass of the plasma torch was carried out. The surface modifications produced in the PE-WPC treated with APPT were assessed by ATR-IR spectroscopy. Figure 6 shows that the ATR-IR spectrum of the PE-WPC treated with APPT at 8 m/min (i.e. short treatment time) is very similar to that of the as-received material. By decreasing the platform speed to 1-2 m/min, i.e. by increasing the treatment time, an increase of the intensity of the bands of the methylene groups of the polyethylene at 2830-2945 and 1445-1460 cm^{-1} and a decrease of the intensity of the OH band of the wood component at 3330 cm^{-1} are noticed, indicating that the surface of the PE-WPC treated with APPT is enriched in polymer. Furthermore, the ATR-IR spectra of Figure 6 suggests some oxidation in the APPJ treated PE-WPC because of the creation of two new bands at 1254 and 1735 cm^{-1} due to the formation of new C-O-C and C=O

groups respectively; the presence of these new bands is more marked in PE-WPC treated with APPT at 1-2 m/min.

The creation of polar groups on the APPT treated PE-WPC surface should lead to an increase in its surface energy, and the increase should be produced mainly in the polar component of the surface energy. The Owens-Wendt approach was used in this study for monitoring the variation in surface energy and their components of PE-WPC after APPT treatment. Figure 7 shows the variation of the surface energy and the dispersive and polar components of the APPT treated PE-WPC as a function of the platform speed. By using platform speeds lower than 8 m/min, a noticeable increase in surface energy is produced due to the creation of polar groups that are responsible for the increase in the polar component of the surface energy; the highest value of the surface energy (65 mJ/m^2) is obtained by treating the PE-WPC surface with APPT using platform speeds of 0.5-2 m/min. This value of surface energy is high and it is consistent with the one obtained in PE-WPC treated with another atmospheric plasma source [12]. On the other hand, the dispersive component of the surface energy of the APPT treated PE-WPC surface is relatively similar irrespective of the platform speed, whereas the values of the polar component of the surface energy vary between 5 and 36 mJ/m^2.

The topography of the PE-WPC surface is also changed by treatment with APPT. Figure 8 shows that the APPT treatment decreases noticeably the roughness of the surface, and the lower is the platform speed, the more pronounced is the smoothening of the surface. In other words, the increase of the treatment time causes a more marked ablation of the APPT treated PE-WPC surface. Thus, the APPT treatment at 8 m/min produces the partial

removal of the wood component on the PE-WPC surface, and some filaments of polyethylene are exposed to a greater extent by decreasing the speed of the platform (i.e. by increasing the treatment time). The exposed polymer on the surface can be oxidized by APPT treatment and new carbon-oxygen polar groups created which should increase the surface energy and the adhesion of PE-WPC.

180º peel tests of the as-received and APPT treated PE-WPC/adhesive tape joints were carried out for determining the optimal experimental variables of APPT treatment. Figure 9 shows the variation of the 180º peel strength values as a function of the platform speed. The variation of the 180º peel strength and the surface energy as a function of the time of treatment is similar, i.e. the APPT treatment increases the 180º peel strength of the joints made with PE-WPC, the highest values are obtained by using platform speeds of 0.5-2 m/min (a three-fold increase in 180º peel strength is obtained). This increase in 180º peel strength can be ascribed to the creation of polar moieties and the increase in the polar component of the surface energy, and to the decrease in roughness that will favour the mechanical interlocking between the acrylic adhesive on the tape and the PE-WPC surface. On the other hand, the moderate increase in 180º peel strength produced in the joints made with APPT treated PE-WPC by using high platform speeds (4-8 m/min) can be ascribed mainly to the reduction of roughness that should contribute less to the mechanical interlocking with the acrylic adhesive.

The best experimental conditions for APPT treatment of PE-WPC leading to the highest hydrophilicity and 180º peel strength values are WPC surface-nozzle distance of 1 cm and platform speed of 1 m/min. Therefore, all WPCs made

with different polymers were treated with APPT by using these optimal conditions.

Figures 10a, 10b and 10c compare the ATR-IR spectra of the as-received and APPT treated (1 cm; 1 m/min) PE-WPC, PP-WPC and PVC-WPC respectively. APPT treatment modifies the chemistry of the WPC surfaces in a different manner depending on the nature of the polymer matrix. The treatment of the PE-WPC with APPT causes an increase of the intensity of the polyethylene bands in the ATR-IR spectrum, a decrease of the intensity of the -OH band of the wood component, and the creation of new bands at 1254 and 1735 cm^{-1} due to the formation of new C–O-C and C=O groups respectively (Figure 10a). On the other hand, APPT treatment of PP-WPC produces a slight increase in the intensity of the methyl and methylene bands at 1376-1455 cm^{-1} due to polypropylene, and more pronounced surface oxidation is noticed in the ATR-IR spectrum which is evidenced by the formation of two new C=O bands at 1731 and 1634 cm^{-1} (Figure 10b). Furthermore, APPT treatment of PVC-WPC causes the reduction of the intensity of the OH band at 3313 cm^{-1} and the O-C-O band at 1094 cm^{-1} due to the wood component in the ATR-IR spectrum, and the creation of a new band at 1732 cm^{-1} due to C=O groups resulting from surface oxidation (Figure 10c).

The surface topography and roughness of the APPT treated WPCs were assessed by SEM. Figure 11 compares the SEM micrographs of the as-received and APPT treated (1 cm; 1 m/min) WPCs. APPT treatment of PE-WPC and PP-WPC causes surface ablation exposing the polymer at the surface and, as a consequence, a reduction in roughness is produced. However, APPT

treatment of PVC-WPC increases the number and size of holes on the surface, and although the surface is relatively smooth, some roughness is created.

The influence of the APPT treatment on the surface energy values of the WPCs can be seen in Table 4. APPT treatment increases the surface energy of all WPCs, more noticeably in PE-WPC, and the increase is due to the increase in the polar component of the surface energy. Therefore, the increase in the surface energies of the APPT treated WPCs can be ascribed to the creation of new polar carbon-oxygen groups.

Because of the increase in the surface energy, the creation of new polar moieties and the changes in the topography of the WPCs by treatment with APPT, an increase in their adhesion can be anticipated. Table 5 shows a substantial increase in 180º peel strength in APPT treated PE-WPC/adhesive tape and APPT treated PP-WPC/adhesive tape joints. However, the 180º peel strength value is similar in the joints made with the as-received and the APPT treated PVC-WPC likely due to the small changes in surface topography (Figure 11).

3.3. Adhesion of APPT treated WPCs to coatings

The adhesion obtained by 180º peel tests in the APPT treated WPC/adhesive tape joints was not optimal because of the poor wettability of the acrylic tape and its permanent adhesion, i.e. the acrylic adhesive tape is a pressure sensitive adhesive that doesn't cure. Therefore, for assessing the influence of the APPT treatment on the adhesion of the WPCs, additional adhesion tests were carried out using two polar adhesives of different nature (waterborne poly(vinyl) acetate adhesive - PVA – and solvent-born polyurethane adhesive –

PU). Because of the solvents in these adhesives, the wettability of the WPC surface will be favoured with respect to that of the solid acrylic tape, and higher values of adhesive strength should be obtained. The adhesive strength of the as-received and APPT treated WPC/adhesive joints were measured by using the cross hatch test.

Figure 12a shows the aspect of the as-received and APPT treated WPC coated with poly(vinyl) acetate adhesive after adhesion test and the cross hatch adhesion values are given in Table 6. Because of their surface roughness, the cross-hatch adhesion of the as-received PE-WPC and PP-WPC is good (a value of 4B according to ASTM D3359 standard is obtained, i.e. no coating square is detached but deep scratched lines can be noticed on the surface). APPT treatment of PE-WPC and PP-WPC increases their cross-hatch adhesion to a value of 5B, i.e. the coating is not detached and the deep scratched lines are not noticed. The improved cross-hatch adhesion of the poly(vinyl) acetate coating to APPT treated PE-WPC and PP-WPC can be ascribed to the increase in surface energy and polarity produced by the treatment. However, the cross-hatch adhesion of the poly(vinyl) acetate coating on the as-received PVC-WPC is quite poor and a value of 0B is obtained because most of the coating is detached (Figure 12a). The cross hatch adhesion of the poly(vinyl) acetate coated APPT treated PVC-WPC increases to a value of 2B because of the moderate increase in the surface energy and in the polarity caused by the treatment.

Figure 12b shows the aspect of the as-received and APPT treated WPC coated with polyurethane adhesive after adhesion test, and the cross hatch adhesion values are given in Table 6. The cross hatch adhesion of the polyurethane

coated as-received PE-WPC and PP-WPC is not good - values of 2B and 3B are obtained respectively, i.e. some coating squares are detached from the surface. Because of the lower surface tension of the polyurethane adhesive with respect to that of the poly(vinyl) acetate adhesive, lower adhesion is obtained in the joints made with the as-received PE-WPC and PP-WPC. However, after APPT treatment and because of the increase in polarity and surface energy produced in PE-WPC and PP-WPC, the cross hatch adhesion of the polyurethane coated APPT treated WPCs increases notably to 5B, i.e. all coating remains on the surface. As for the poly(vinyl) acetate coating, the adhesion of the polyurethane coating to the as-received PVC-WPC is quite poor and a value of 0B is obtained (Figure 12b). However, the cross hatch adhesion of the polyurethane coated APPT treated PVC-WPC increases to a value of 5B indicating a substantial improvement in adhesion.

4. CONCLUSIONS

APPT treatment improved noticeably the adhesion of the WPCs made with different polymers, mainly PE-WPC, to coatings of different chemical nature. The optimal conditions of the APPT treatment were WPC surface-nozzle distance of 1 cm and platform speeds of 0.5-2 m/min. The increase in adhesion of the WPCs was ascribed to the removal of the wood component and the exposure of polymer at the surface that led to the creation of new carbon-oxygen polar groups on the polymer surface and to the increase in their surface energy. The changes in surface topography of the WPCs had some influence in determining the extent of mechanical interlocking between the coating and the WPC surface. Finally, the less marked increase in adhesion corresponded to

the joints made with PVC-WPC because of the slight improvement in surface energy and polarity caused by the APPT treatment.

Acknowledgments. Financial support from Spanish Ministry of Economy and Competitiveness – INNPACTO project grant no. IPT-2011-1454-020000 – is acknowledged.

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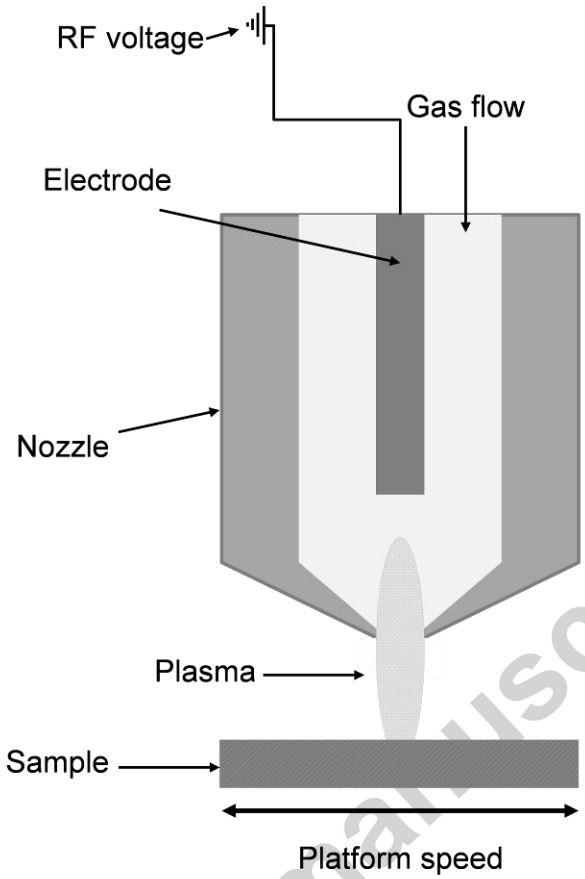


Figure 1. Scheme of the APPT equipment.

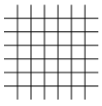
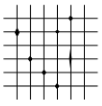
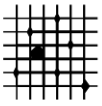
Surface cross-cut area from which flaking has occurred. (6 parallel cuts).						
Classification	5B (0%)	4B (<5%)	3B (5-15%)	2B (15-35%)	1B (35-65%)	0B (>65%)

Figure 2. Cross hatch adhesion scale for coatings according to ASTM D3359 standard.

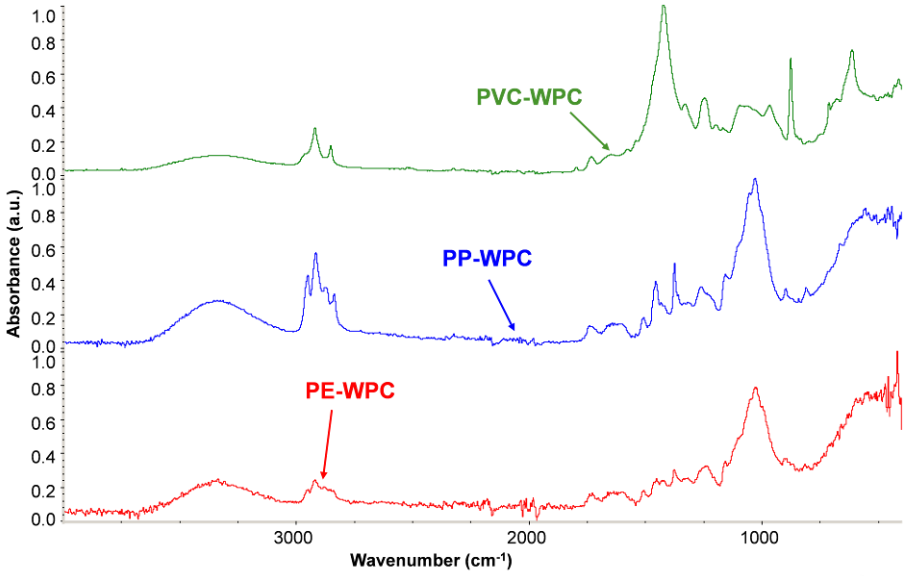


Figure 3. ATR-IR spectra of the as-received WPCs. Diamond prism.

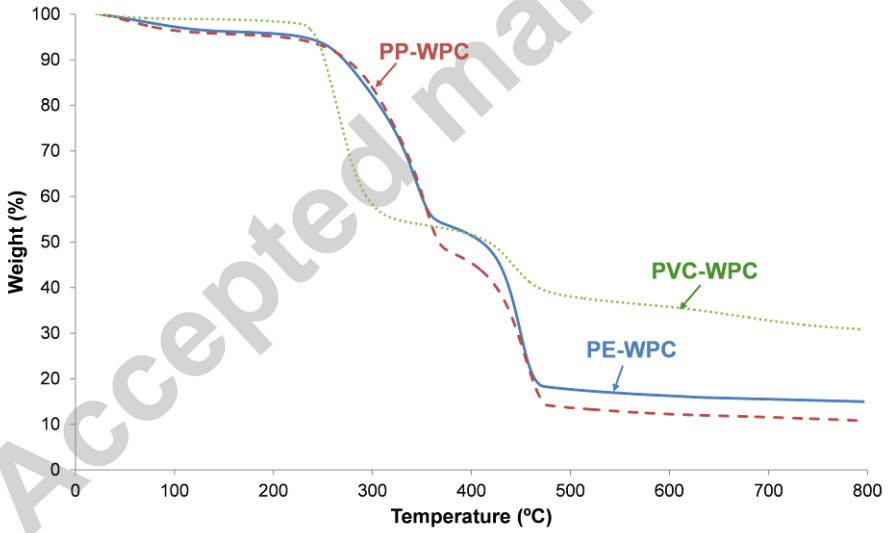


Figure 4. Variation of the weight as a function of the temperature for the as-received WPCs. TGA thermogram. Nitrogen atmosphere.

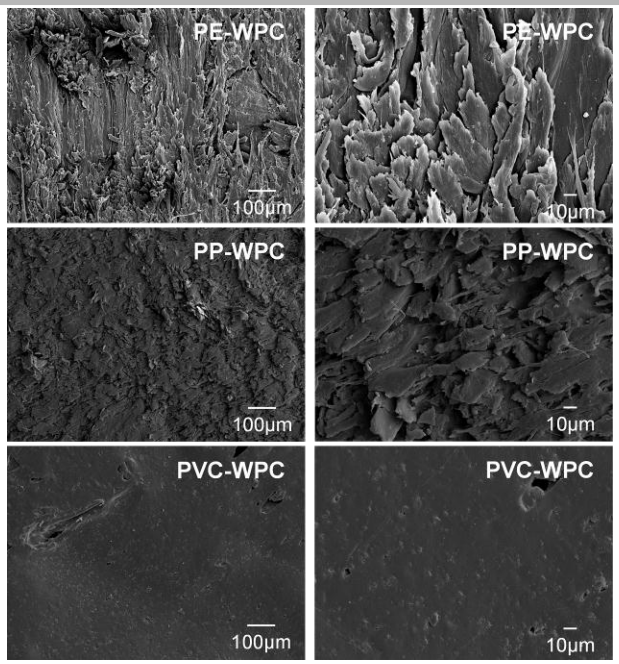


Figure 5. SEM micrographs of the as-received WPCs.

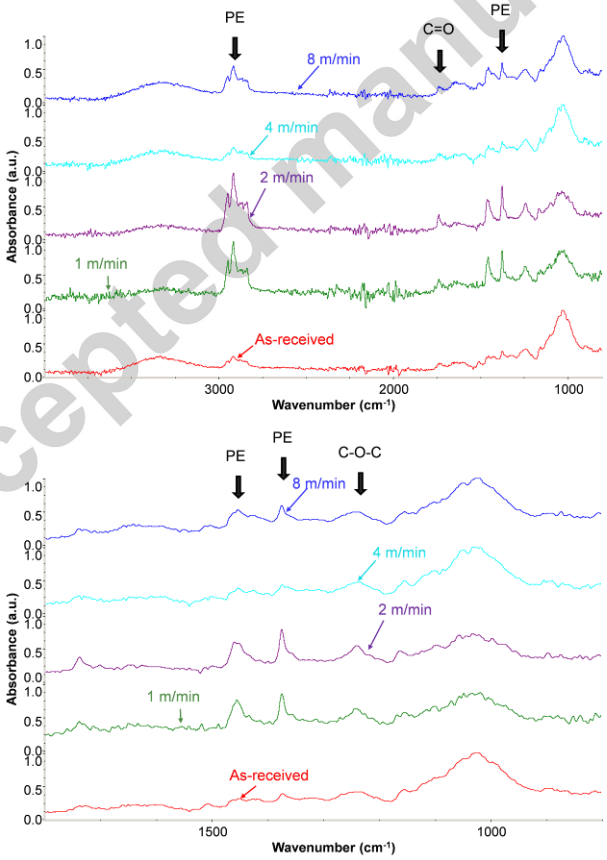


Figure 6. ATR-IR spectra of the as-received and APPT treated PE-WPC.

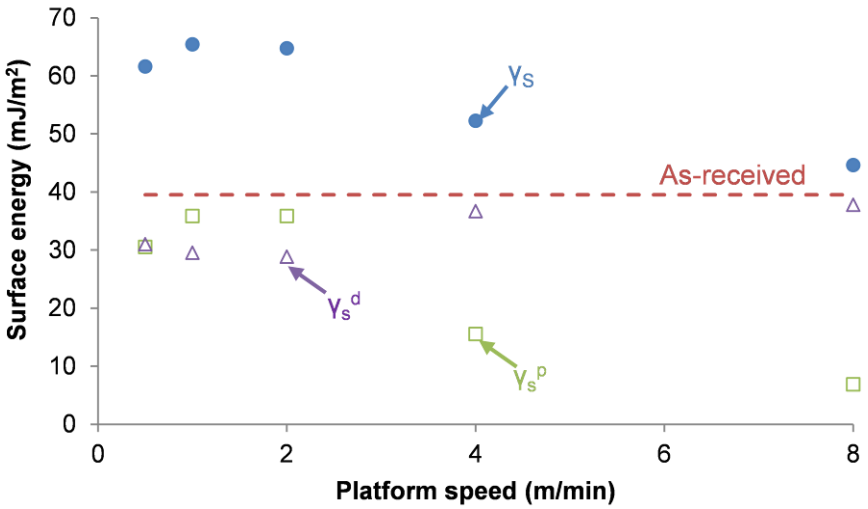


Figure 7. Variation of the total surface energy and their dispersive and polar components of the as-received and APPT treated PE-WPC as a function of the speed of the platform. WPC surface-nozzle distance: 1 cm.

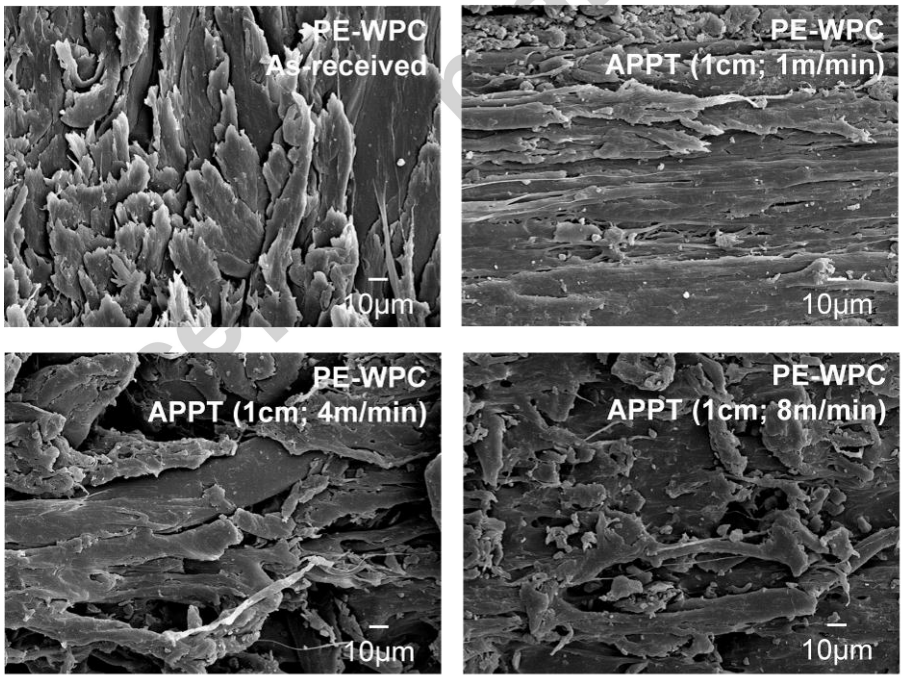


Figure 8. SEM micrographs of the as-received and APPT treated PE-WPC. Influence of the speed of the platform. WPC surface-nozzle distance: 1 cm.

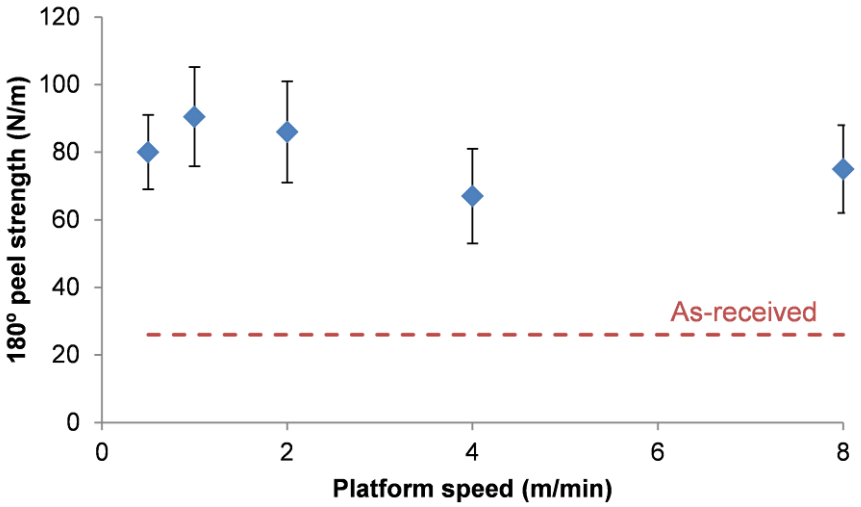


Figure 9. Variation of the 180º peel adhesive strength of APPT treated PE-WPC/adhesive tape joints as a function of the speed of the platform. WPC surface-nozzle distance: 1 cm. An adhesion failure was always obtained.

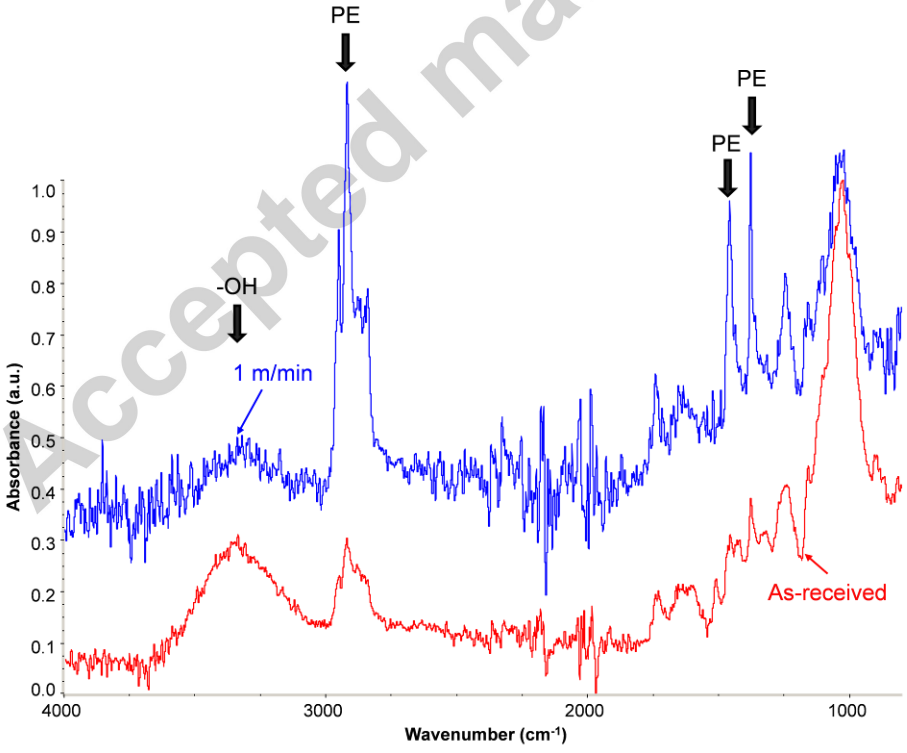


Figure 10a. ATR-IR spectra of the as-received and APPT treated (1 cm; 1 m/min) PE-WPC.

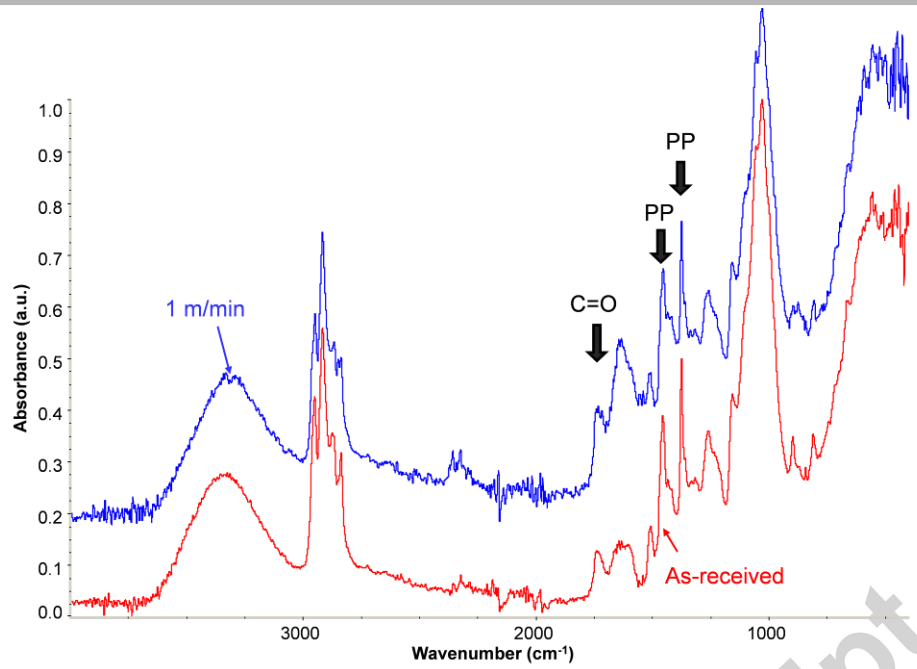


Figure 10b. ATR-IR spectra of the as-received and APPT treated (1 cm; 1 m/min) PP-WPC.

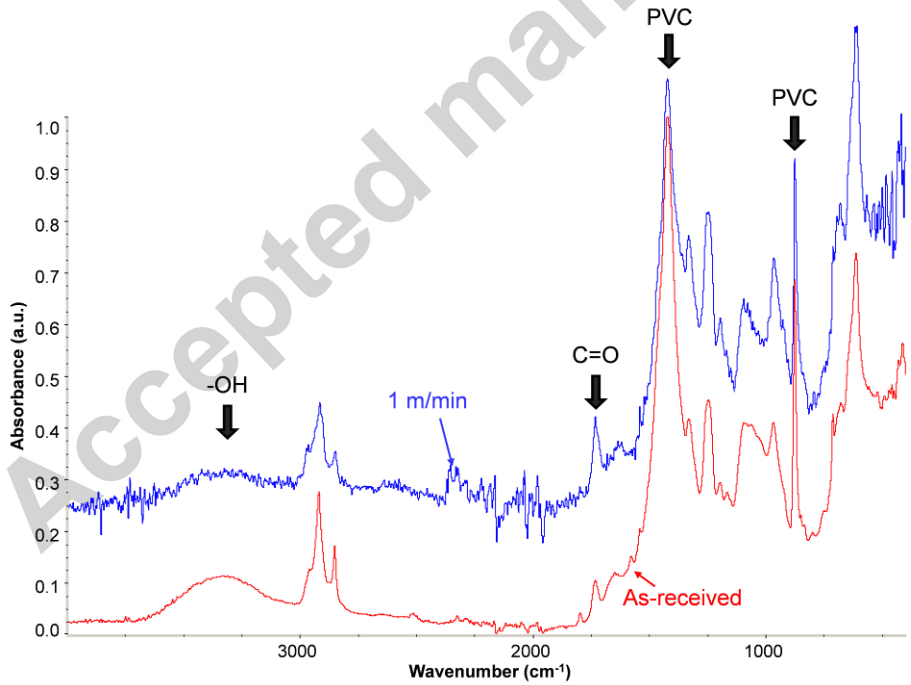


Figure 10c. ATR-IR spectra of the as-received and APPT treated (1 cm; 1 m/min) PVC-WPC.

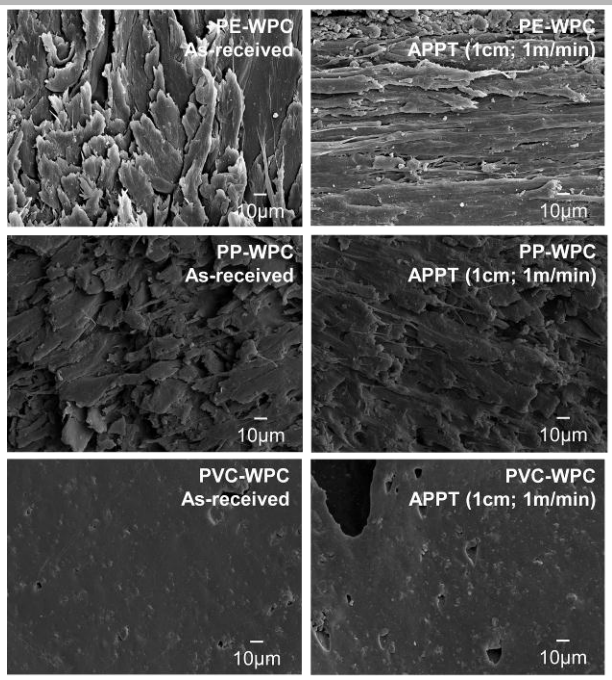


Figure 11. SEM micrographs of the as-received and APPT treated (1cm; 1 m/min) WPCs.

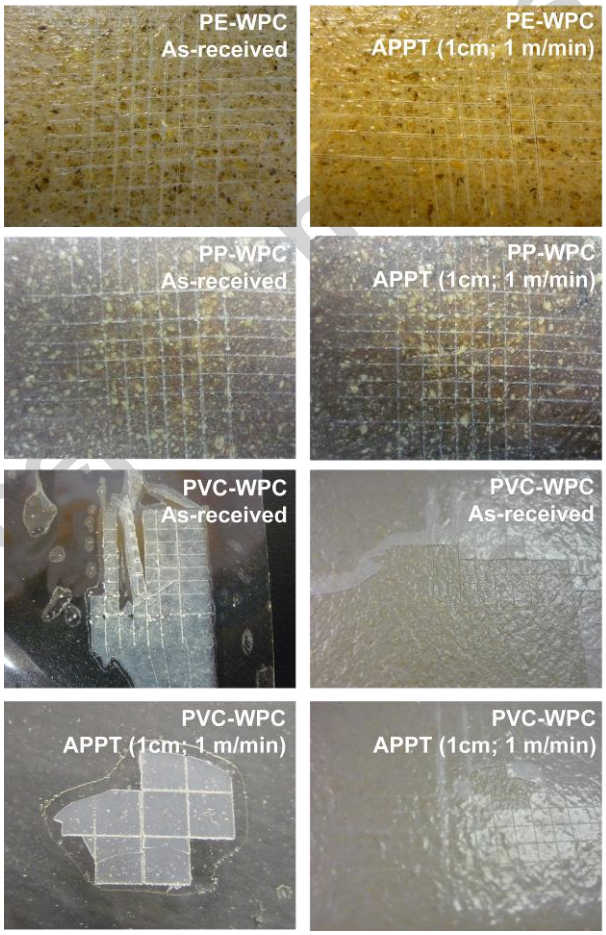


Figure 12a. Photos of the poly(vinyl) acetate coated WPC surfaces after cross-hatch test.

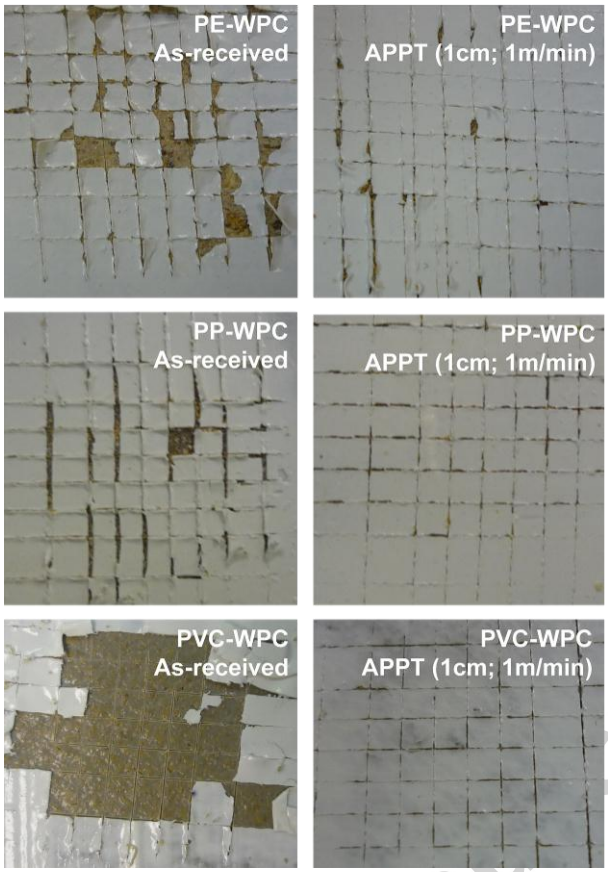


Figure 12b. Photos of the polyurethane coated WPC surfaces after cross-hatch test.

Table 1. Wood index values of the as-received WPCs.

WPC	Wood Index
PE-WPC	332
PP-WPC	179
PVC-WPC	60

Table 2. Temperatures and weight losses of the different thermal decompositions of the as-received WPCs. TGA experiments.

	PE-WPC		PP-WPC		PVC-WPC	
Compound	**T_1 (ºC)**	**Weight $loss_1$ (%)**	**T_2 (ºC)**	**Weight $loss_2$ (%)**	**T_3 (ºC)**	**Weight $loss_3$ (%)**
Water	70	4	159	4	31	1
Wood	345	43	328	42	279	28
Polymer	449	37	454	36	441	34
CO_2	-	-	-	-	684	6
Residue (N_2 atm.)	800	16	800	14	800	31

Table 3. Values of the contact angles (25ºC) and the total surface energy, and their polar and dispersive components, of the as-received WPCs.

WPC	Contact angle (degrees)		Surface energy (mJ/m^2)		
	H_2O	CH_2I_2	γ_S^p	γ_S^d	γ_S
PE-WPC	105	34	0	39	39
PP-WPC	111	65	0	26	26
PVC-WPC	83	65	7	21	28

Table 4. Total surface energy and their polar and dispersive components of the as-received and APPT treated (1cm; 1m/min) WPCs.

WPC	Surface energy (mJ/m^2)					
	As-received			APPT (1cm; 1m/min)		
	γ_S^p	γ_S^d	γ_S	γ_S^p	γ_S^d	γ_S
PE-WPC	0	39	39	36	29	65
PP-WPC	0	26	26	26	18	44
PVC-WPC	7	21	28	23	23	46

Table 5. 180º peel strength values of the as-received and APPT treated WPC/adhesive tape joints.

WPC	180º peel strength (N/m)	
	As-received	APPT (1cm; 1m/min)
PE-WPC	26	90
PP-WPC	90	196
PVC-WPC	59	52

Table 6. Cross hatch adhesion of poly(vinyl) acetate (PVA) and polyurethane (PU) coated WPCs. ASTM D3359 standard.

WPC	Cross hatch adhesion (a.u.)			
	As-received		APPT (1cm; 1m/min)	
	PVA	PU	PVA	PU
PE-WPC	4B	2B	5B	4B
PP-WPC	4B	3B	5B	5B
PVC-WPC	0B	0B	2B	5B